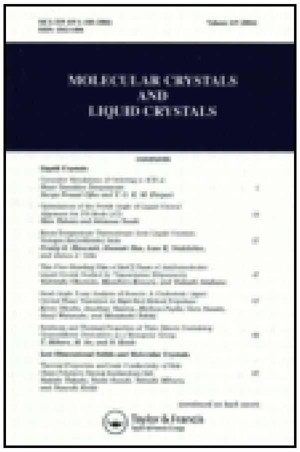

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STABLE IMIDAZOLINE NITROXIDES FOR COORDINATION CHEMISTRY

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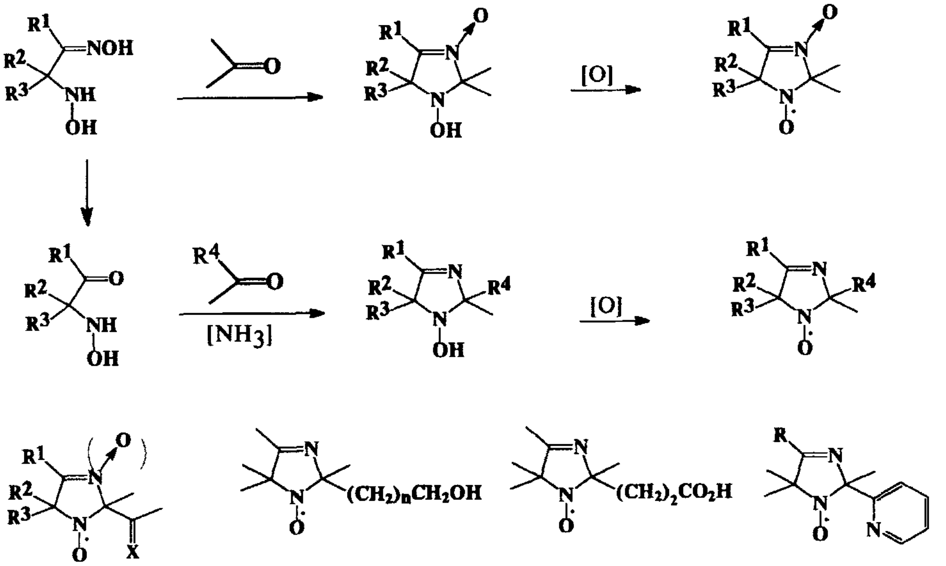
Abstract: Structures of stable imidazoline nitroxides that are of interest for coordination chemistry and as a precursors of magnet materials are discussed.

The different approaches to the fully or partially organic magnetic materials have been worked out during last ten years. Usually they are based on the design of heteropolyspin systems, in which the paramagneric centers of different nature are situated in definite order and there is an efficient exchange interaction between them. There are two main synthetic routes for the construction of these systems: a design of the complexes of different paramagnetic metal ions with diamagnetic ligands or of the complexes of diamagnetic or paramagnetic metal ions with the paramagnetic ligands. Evidently, the most suitable paramagnetic ligands for these purposes are stable nitroxides (SN), molecule of which contains paramagnetic center, a nitroxyl group along with additional donating functional group or groups which provides coordination with central nucleus. Advances of the synthetic chemistry of SN now permits synthesis of wide variety of nitroxyl containing molecules that are differ in a topology and a nature of additional functional groups.[1]

One of the most promising type of paramagnetic ligands is stable imidazoline nitroxides (IN).[2,3] The reason of this is an additional functional group - imino group or nitrone group in the heterocycle, which are on the one hand capable of forming of a bonds with metal ions. On the other hand they permit different chemical transformations of these SN to introduce a wide scope of functional groups onto a molecule that could provide complexing. An another peculiarity of this type of SN is a possibility of introducing of additional functional group on the stage of heterocycle formation.

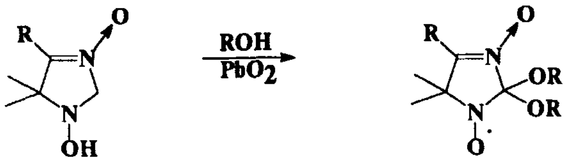
Scheme 1

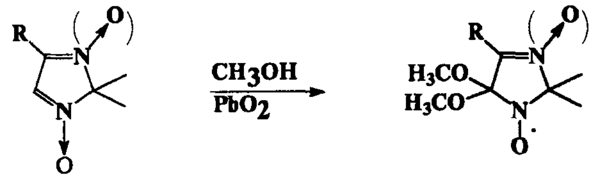


X = NOH, HOH, NNHCH$_3$, NNHCONH$_2$
NNHCSNH$_2$

During last ten years a method for the synthesis of SN with the substituents that are differ from alkyl or aryl group in the nearest environment of nitroxyl group was found. This method is based on the oxidative alkoxylation of heterocyclic nitrones or their precursors and provides synthesis of IN with alkoxy groups in the 2 or 5 position of imidazoline heterocycle.[4-6]

Scheme 2

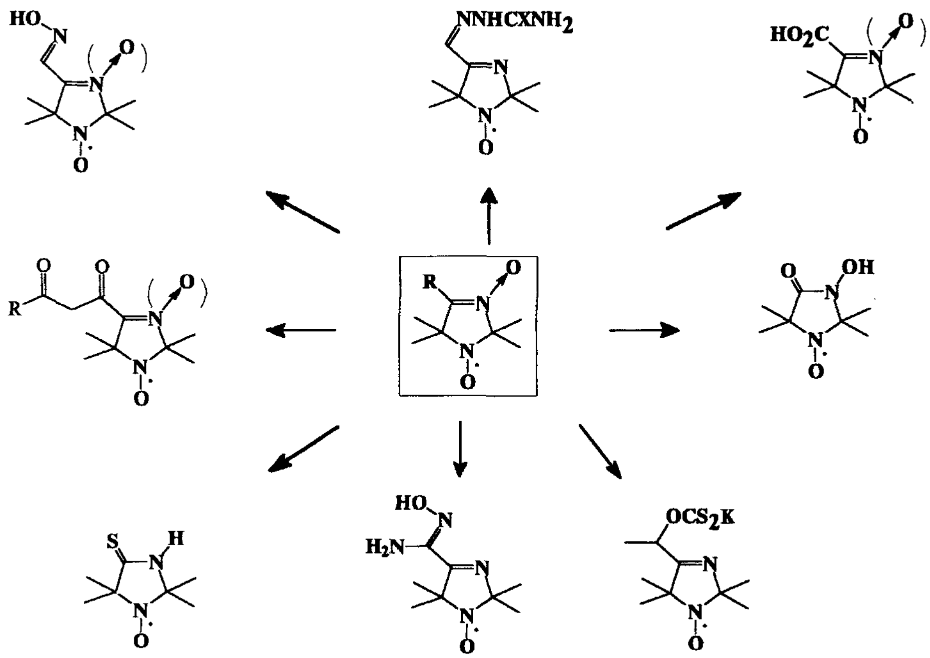




Imidazoline SN with alkoxy groups at α-carbon of nitroxyl group are of high stability that is close to the stability of an ordinary tetraalkyl substituted nitroxides that permits different chemical transformations with retain of nitroxyl group. It should be noted that the presence of the alkoxy groups in the molecule noticeably changes physical properties of these nitroxides, in particularly influences on the spin density delocalization in the heterocycle.[7]

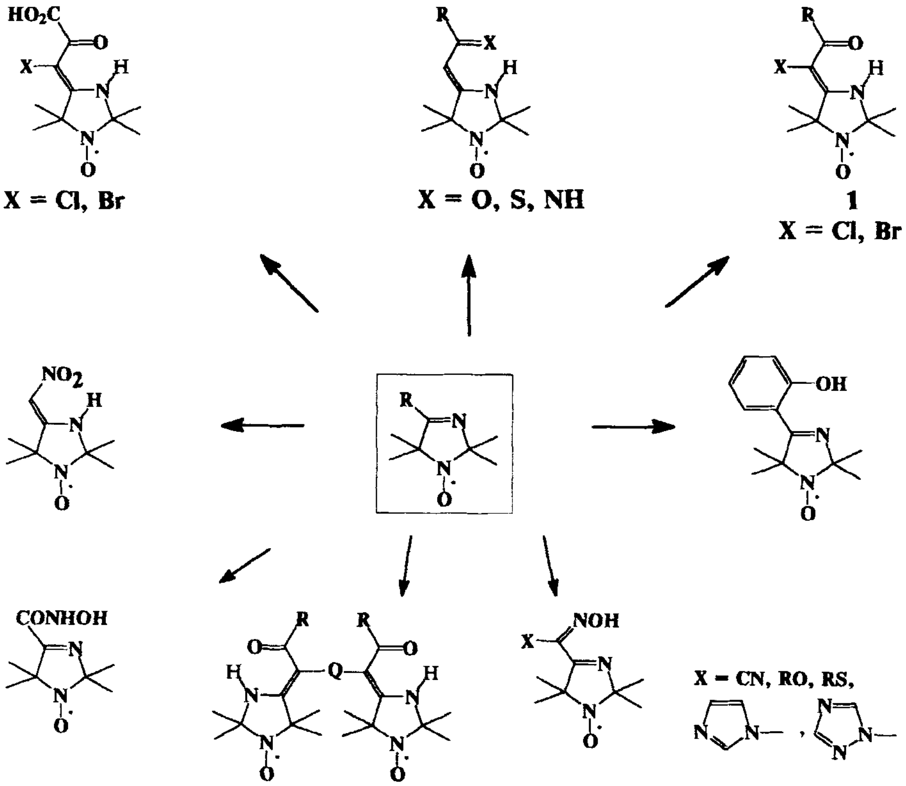
Reactivity of the nitrone group in the 3-imidazoline-3-oxide molecule (Scheme 3) or the imino group in the 3-imidazoline molecule (Scheme 4) provides synthesis of various SN of 3-imidazoline-3-oxide, 3-imidazoline and imidazolidine series capable of chelating.[1-3]

Scheme 3



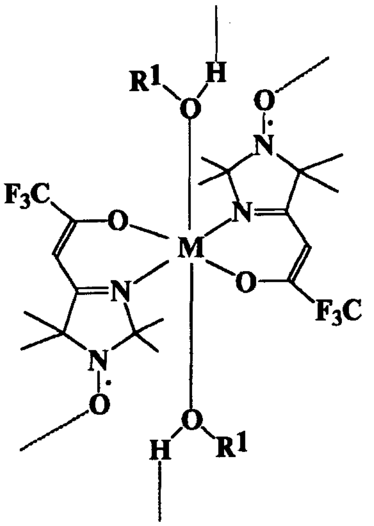
Historically, some of the SN in Schemes 3 and 4 were used in the synthesis of complexes with transition metal ions, but a profound investigation of these complexes were not carried out. The data about complexes synthesized were published in a review.[8] Later it was suggested to use SN capable of chelating as an analytical reagents for determination of concentration of paramagnetic and especially diamagnetic metal ions by means of EPR spectroscopy.[9]

Scheme 4



An attention paid to the coordination compounds with paramagnetic ligands, IN , was grown during few last years due to the phenomena of low-temperature magnetic phase transfer to the ferromagnetic state that was found for some enaminoketonates of type (1). The data concerning these and relative problems summarized on a reviews.[10-12] In particularly, it was shown that enaminoketonates form three-dimensional regular structure that possesses macromolecular magnetism (Structure 1).

Structure 1.



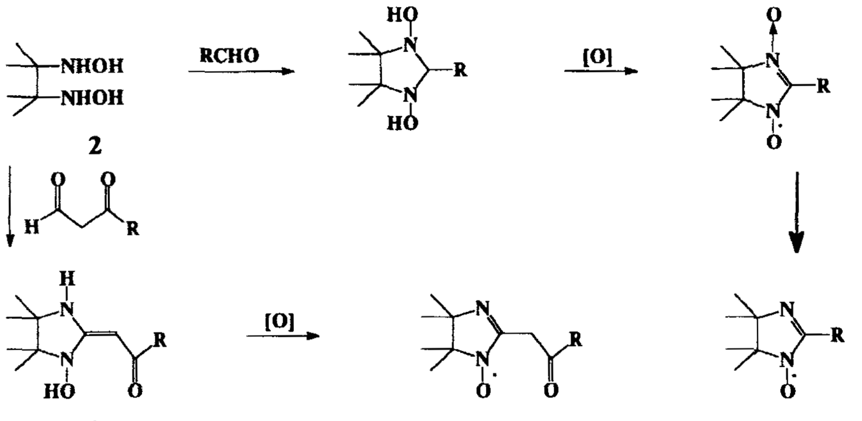
The reason of the possibility of design of molecular magnets based on complexes of SN with metal ions is due to the efficient spin exchange interaction through the imidazoline heterocycle. The nature of this phenomena is unknown up to now. Evidently an important role in the exchange interaction have an electron orbitals of central nucleus of complex because the delocalization of spin density in the molecule of a ligand on the atoms remote from nitroxyl group is insignificant especially in the case of 3-imidazoline derivatives. More efficiently spin density spreads through the 3-imidazoline-3-oxide heterocycle,[7] but for the coordination compounds there is a reverse trend, *i.e.* the exchange interaction is more efficient in the case of ligands containing no N-oxide oxygen atom.[10] It should be noted, that electron withdrawing substituents in the 2 and 5 position of imidazoline heterocycle noticeably changes an efficiency of spin conductivity through the imidazoline fragment both in the ligand and in the complex.[10]

As could be expected exchange interaction is the most efficient in the case of SN of 2-imidazoline and 2-imidazoline-3-oxide series where imino or nitrone group is on the direct conjugation with the nitroxyl group.[11,12] In this connection the use of SN of this type as a precursors for the design of molecular based magnets seems to be most promising. But for this series of nitroxides there are some complexities of synthetic nature, that do not permit a varying of a character and a position of substituents in the cycle.

The possibility for functionalization of these nitroxides is based on either a modification of the substituent R in the 2 position of heterocycle or an involving into the condensation reaction leading the heterocycle formation of the aldehydes with appropriate subsituent, bearing desirable functional group. But even in this case the possibilities are limited because of the low stability of these nitroxides (for example R = CH_2OH, CO_2H, etc.).[13]

Recently it was found that the condensation reaction of bishydroxylamine (**2**) with β-ketoaldehydes gives 1-hydroxyimidazolidines (**3**), which could be considered as an analogue of enaminoketones of 3-imidazoline series **1** and a precursors of SN of 2-imidazoline. It was shown, however, that corresponding nitroxides are not stable and they were failed to be isolated in pure state.[14] Never the less the possibility of the synthesis of a complexes of these nitroxides with transition metal ions now are in progress.

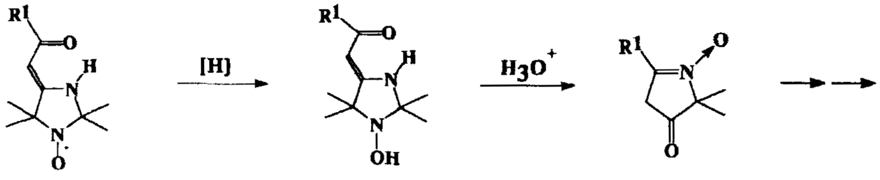
Scheme 5.

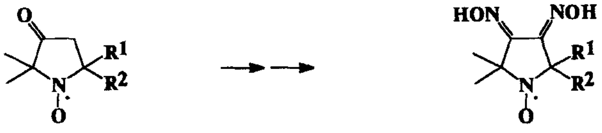


R = alkyl, aryl,
α-, β-, γ-pyridyl

One more important feature of imidazoline heterocycle with suitable substituents is their ability to be transformed into nitroxides of pyrrolidine series.[15,16]

Scheme 6.





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An EPR behavior of some dioximates of SN (**4**) has been investigated in the solutions and was shown that pyrrolidine ring also permits efficient spin density conductivity and the value of exchange interaction grows sharply with the increase of electron withdrawing ability of subsituent in the 2 position of heterocycle.[17] Synthesis of crystalline phases of dioximates and investigation of their structural and magnetic peculiarities now is continued and results should be published elsewhere.

Thus imidazoline nitroxides seemed to be very important class of paramagnetic ligands - precursors of molecular magnets. The chemistry of this SN now is developed and its advance promises synthesis of a new interest ligands for coordination chemistry.

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